Poly(allyl Glycidyl Ether)-A Versatile and Functional Polyether Platform

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ABSTRACT: Allyl glycidyl ether, polymerized from potassium alkoxide/naphthalenide initiators under both neat and solution conditions was shown to be a highly controlled process. In both cases, molar masses (10–100 kg/mol) were determined by the reaction stoichiometry, and low polydispersity indices (1.05–1.33) could be obtained with a full understanding of the dominant side reaction, isomerization of the allyl side chain, being developed. The degree of isomerization of allyl to *cis*-prop-1-enyl ether groups (0–10% mol) was not correlated to the molar mass or polydispersity of the polymer but was dictated by the polymerization temperature. This allows the extent of isomerization to be reduced to essentially zero under either melt or solution conditions at polymerization temperatures of less than 40 °C. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 4498–4504, 2011

KEYWORDS: anionic polymerization; polyethers; ring-opening polymerization

INTRODUCTION Polyethers, such as poly(ethylene glycol) (PEG), are widely used materials in commercially established fields such as drug-delivery,[1] and control of biocompatibility,[2] and are becoming increasingly important in emerging technologies such as dye-sensitized solar cells,[3] and lithium-polymer batteries.[4] A fundamental challenge with all PEG-based systems is the lack of functional handles along the polymer backbone which limits the modification and tunability of this valuable materials platform.[5] As a functional alternative to PEG in some applications, low-T_g poly(allyl glycidyl ether) (PAGE) has been examined due to its inherent chemical flexibility stemming from the pendant allyl groups. For example, the allyl-ethers along the PAGE backbone are amenable to thiol-ene radical coupling chemistry which enables the elaboration of PAGE with a wide variety of functionalities without the need for tedious protection–deprotection chemistries.[6] Such modular and facile reactivity increases the relevance of PAGE for applications in therapeutics, bioconjugation, and polymer-supported catalysis.[7,8] This combination of latent chemical functionality, and inherent physical properties (low T_g, lack of crystallinity) makes a compelling case to systematically explore the synthesis and reactivity of this potentially useful and inexpensive polyether materials platform.

Examples of the polymerization of AGE,[9,10] and the selective functionalization of its pendant allyl groups by thiol-ene radical coupling can be found in the literature.[11–13] Erberich et al.[10] carried out an extensive analysis of the polymerization chemistry of AGE and the functionalization, protection, and allyl-deprotection to linear polyglycidol. However, the authors concluded that the polymerization of allyl glycidyl ether (AGE) was only controlled to 80% conversion with termination by abstraction of an allylic proton competing with propagation. Hrubý et al.[11] also investigated the application of poly(ethylene oxide)-*b*-poly(allyl glycidyl ether) (PEO-PAGE) as a micellar drug delivery vehicle with doxorubicin units being randomly attached, via pH-sensitive hydrazone linkages, along the PAGE block. Similarly, Persson and Jannasch synthesized a poly(allyl glycidyl ether)-*b*-poly(ethylene oxide)-*b*-poly(allyl glycidyl ether) (PAGE-PEO-PAGE) triblock copolymer and graft copolymers of PAGE on a poly(p-hydroxy styrene) backbone. In these cases, thiol-ene coupling of benzimidazole units to the PAGE blocks creates robust proton-exchange membrane materials for hydrogen fuel-cell applications.[12] The challenge with these studies is that the polymerization of AGE under the reported conditions results in significant termination and other side reactions with impure block copolymers being obtained that required removal of PEO and PAGE homopolymer contaminants. Alternatively, Hu et al.[14] have polymerized AGE to low molar

masses (2–4 kg/mol) using a sodium ethoxide initiator and xylene as the polymerization solvent. The molar masses agreed well with the reaction stoichiometry; however, the resultant polydispersity indices (PDIs) were low (1.04–1.08) only at low molecular weights. Obermeier and Frey investigated the copolymerization of ethylene oxide and AGE.[13] However, their analysis was limited to low molecular weights of less than 10 kg/mol and utilized cesium alkoxide initiators that were generated by the deprotonation of an alcohol with cesium hydroxide, followed by removal of water. The molar masses they reported were consistently 10% above that defined by the reaction stoichiometry.

The significant promise shown by PAGE-based materials, coupled with unresolved issues concerning the polymerization of AGE, prompted a thorough reinvestigation of the homopolymerization of AGE. A driving force for this focus on homopolymerization is the ease of handling AGE compared to ethylene oxide with its associated low boiling point and high toxicity which increases the complexity of the polymerization. The use of alternate initiating systems under a wide variety of bulk and solution conditions resulted in optimized polymerization conditions and the development of a fundamental understanding for controlling side reactions in this useful materials platform.

RESULTS AND DISCUSSION

In examining the methods to synthesize PAGE, many of the approaches have relied on the utilization of a strong, nonnucleophilic base and removal of the conjugate acid (e.g., water, or *tert*-butanol) to generate an alkoxide initiator followed by the addition of AGE and polymerization at high temperatures (ca. 100 °C).[9–12] A challenge with these strategies is that protic impurities are introduced during generation of the initiating system and these impurities may be difficult to quantitatively remove, leading to subsequent interference with the polymerization. Moreover, the use of high polymerization temperatures can be detrimental to the polymerization leading to unwanted side reactions.

To overcome these issues, the radical-anion potassium naphthalenide was used to generate a potassium alkoxide initiator which was employed for the polymerization of AGE.[15,16] Significantly, the by-products of deprotonation of the benzyl alcohol initiator with potassium naphthalenide are naphthalene and dihydronaphthalene[13] which are innocuous to the polymerization, and the introduction and removal of residual water or alcohol characteristic of other initiation strategies such as sodium or cesium alkoxides is unnecessary.[9–12] Scheme 1 shows the generation of potassium alkoxide initiator and subsequent polymerization of AGE.

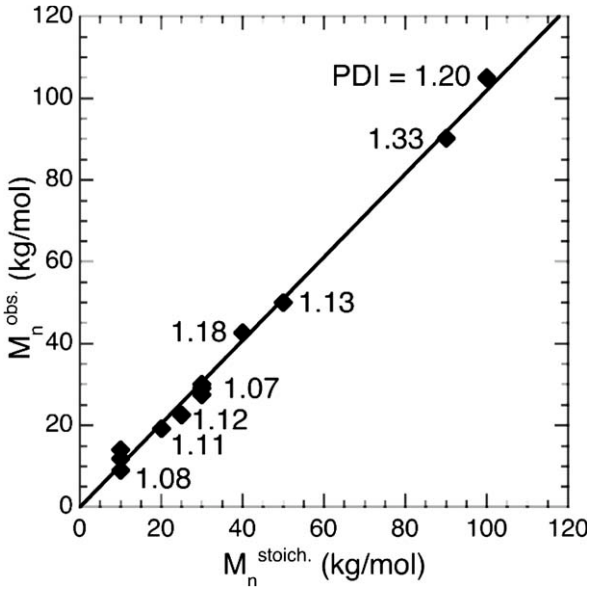
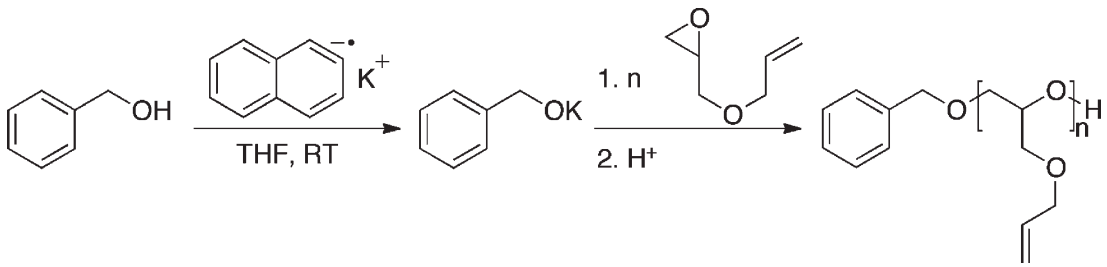


FIGURE 1 Number-average molar mass ($M^{obs.}$) as measured by ^{1}H NMR spectroscopy versus the molar mass defined by the reaction stoichiometry ($M^{stoich.}$). The line plotted alongside the data has a slope of one and an intercept of zero. Polydispersity indices as measured by size-exclusion chromatography are shown adjacent to each data-point. In the case of several closely space data points, the average polydispersity is shown. Detailed polymerization results are shown in Table 1.

In developing a fundamental understanding of the effect of polymerization conditions on the resulting PAGE polymers, polymerizations were conducted over the temperature range, 30–80 °C, both neat and in solution. All polymerizations were carried out for 20 h, which was sufficient time for quantitative conversion of AGE except for the highest molar masses (>50 kg/mol) for which 144 h was used to reach completion. It should be noted that the polymerization of AGE was controlled over an order of magnitude in molar mass (10–100 kg/mol) and under a variety of polymerization conditions. Figure 1 details the observed number-averaged molar mass (M_n^{obs}) plotted versus the molar mass as defined by the reaction stoichiometry (M_n^{stoich}) with number-



SCHEME 1 Polymerization of allyl glycidyl ether from potassium benzoxide.

TABLE 1 Polymerization Results Carried Out Under a Variety of Polymerization Conditions

Samples	M_n^{obs} [a]	M_n^{stoich} [b]	PDI[c]	%Isomer[d]	Solvent[e]	$T_{Polym.}$(°C)
1	9.0	10.0	1.09	0.0	Neat	30
2	11.8	10.0	1.08	8.8	Diglyme	80
3	14.0	10.0	1.08	0.6	Diglyme	40
4	19.2	20.0	1.11	1.3	Neat	60
5	22.5	25.0	1.12	0.0	Neat	30
6	27.5	30.0	1.07	6.3	Neat	80
7	29.1	30.0	1.10	0.0	Diglyme	40
8	30.0	30.0	1.05	2.8	Neat	80
9	42.7	40.0	1.18	0.2	Neat	40
10	50.0	50.0	1.13	5.0	Diglyme	80
11	90.2[f]	90.0	1.33	0.0	Neat	30
12	105	100	1.20	4.0	Diglyme	80

[a] M_n^{obs} measured by NMR spectroscopy.
[b] M_n^{stoich} was defined by the monomer to initiator ratio.
[c] Polydispersity indices were determined by SEC in chloroform relative to polystyrene standards.
[d] The percent *cis*-prop-1-enyl isomer incorporation was determined by ^{1}H NMR spectroscopy.
[e] Solution polymerizations were carried out at 20 wt % monomer in diglyme.
[f] Polymerization time of 144 h.

averaged molar masses being determined by ^{1}H NMR spectroscopy using end group analysis based on the benzylic protons (2H) on the initiator and either allyl (1H) or backbone ether protons (5H) to determine the number of repeat units. In solution and melt polymerizations carried out between 30–80 °C, the resultant molar masses compared well with the monomer to initiator feed ratios as indicated by the close agreement between M_n^{obs} and M_n^{stoich}. PDIs were measured by size exclusion chromatography (SEC) relative to polystyrene standards and were typically between 1.05 and 1.20 with higher polydispersities only being observed for high molecular weight materials (Fig. 1). These increases in PDI are due to chain coupling occurring after complete consumption of AGE or radical coupling of backbone allyl substituent, rather than any transfer or termination reactions competing with propagation at high conversion as noted by Erberich et al.[10]

Hans et al.[17] reported a chain-transfer reaction in ethoxy ethyl glycidyl ether (EEGE) polymerizations beginning with the abstraction of a methylene proton adjacent to the epoxide ring by an active alkoxide chain-end. Subsequently, the epoxide ring opened introducing a new alkoxide which reinitiated polymerization. This chain-transfer to monomer generated PEEGE materials with allylic-ether end-groups exhibiting characteristic resonances in the ^{1}H NMR spectra, and molecular weight distributions with long, low-molecular weight tails in the size-exclusion chromatograms. No chain-transfer to monomer was detected in polymerizations of AGE either by ^{1}H NMR spectroscopy or size-exclusion chromatography (Fig. 2).

The controlled nature of this synthetic approach to PAGE then allowed a detailed examination of the relationship between polymer structure and polymerization conditions. A representative ^{1}H NMR spectrum for AGE polymerized at 30 °C (Table 1, entry 5) is shown in Figure 3 (top) along with peak assignments. At lower polymerization temperatures, the repeat-unit structure is derived from the AGE monomer feedstock without isomerization as can be seen by the defined resonances corresponding to the allyl substituent in Figure 3, inset (a). However, at higher polymerization temperatures, the repeat-unit structure can no longer be assigned to a single isomer. PAGE polymerized above 40 °C both neat and in solution exhibits ^{1}H and ^{13}C NMR spectra consistent with isomerization of the allyl repeat unit (Fig. 3, bottom and Fig. 4, respectively). Significantly, peak assignments for the three possible isomers (allyl; *cis*-prop-1-enyl, and *trans*-prop-1-enyl) clearly reveal the presence of the *cis*-isomer and the absence of the *trans*-isomer.[18] Sunder et al.[9] and Obermeier and Frey reported on the presence of prop-1-enyl isomers but identified the isomer as trans, but as shown above only the *cis*-isomer is present.[13] Finally, Erberich et al.[10] reported the termination of AGE polymerizations as possibly occurring through the abstraction of the allylic proton but did not report the presence or formation of the 1-propenyl isomer.

On the basis of the work of Prosser, the isomerization of allyl ethers along the backbone may occur according to Scheme 2.[19] The living potassium alkoxide chain-end abstracts an allylic proton from an AGE repeat unit and the alkyl potassium formed from this proton abstraction reaction coordinates with the potassium counter-ion forming a five-membered ring, stabilizing the *cis*-isomer. The alkyl potassium then deprotonates a dormant alcohol creating a potassium alkoxide chain-end and propagation of AGE continues resulting in a *cis*-propenyl repeat-unit isomer. As a result, this process does not constitute a termination reaction with isomerization being fast relative to propagation as no evidence of

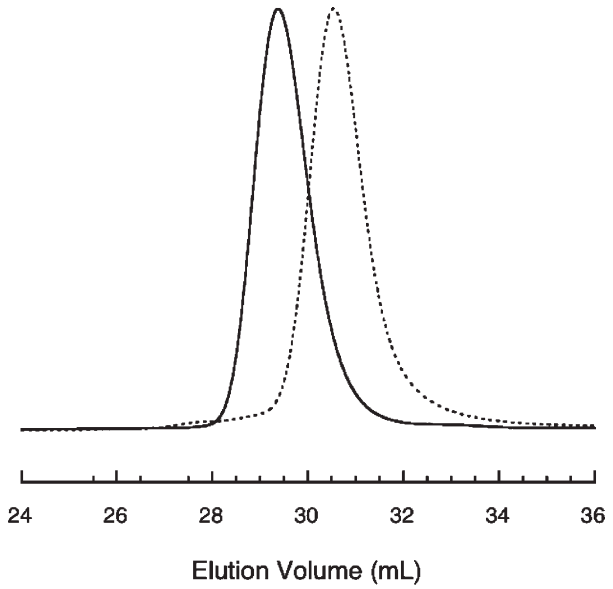


FIGURE 2 Size-exclusion chromatographs of polymers **2** (dashed line, M_n = 11.8 kg/mol, PDI = 1.08) and **6** (solid line M_n = 27.5 kg/mol, PDI = 1.07) as detailed in Table 1.

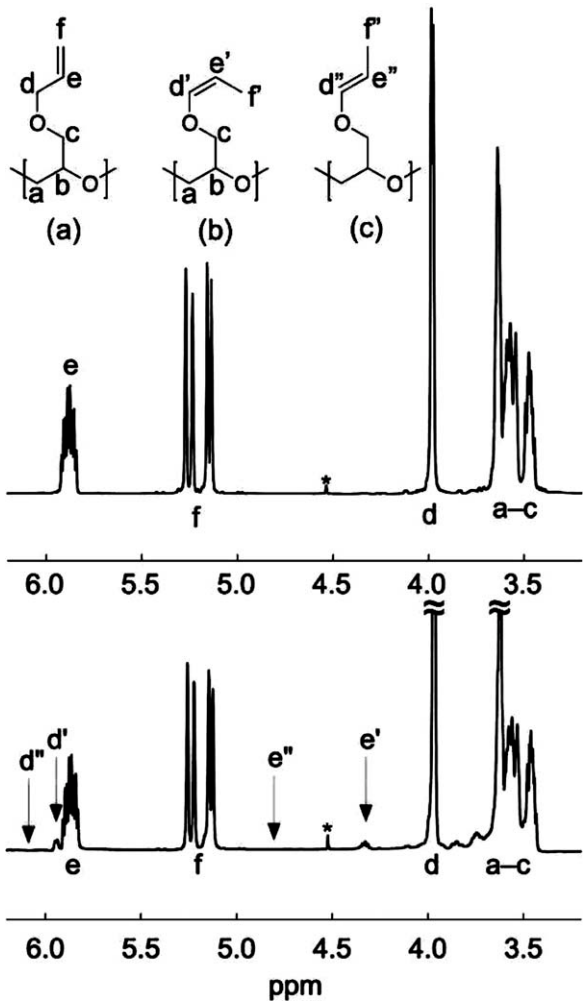


FIGURE 3 (Top spectrum) ^{1}H NMR spectrum of poly(allyl glycidyl ether) polymerized neat at 30 °C (Table 1, entry 5). Peak assignments are shown in the inset. The resonance near 4.5 ppm marked with an asterisk is due to the benzyl (2H) end group protons used for determination of molar mass. (Bottom spectrum) ^{1}H NMR spectrum of PAGE polymerized neat at 120 °C (see Table 2) with inset peak assignments showing the presence of extra resonances due to the presence of *cis*-propenyl isomers. Three possible isomers exist: (a) allyl, (b) *cis*-prop-1-enyl, (c) *trans*-prop-1-enyl. Resonances are observed for the monomer-derived allyl, and *cis*-prop-1-enyl isomers only. No evidence of *trans* isomerization is present.

premature termination or chain-transfer to monomer is seen in the SEC traces (see Fig. 2). In addition, the amount of *cis*-isomer is not correlated with the molar mass or polydispersity; instead, there is a strong correlation with reaction temperature (see Table 1 and Fig. 1). No significant isomerization occurs below a polymerization temperature of 40 °C and the mole fraction of isomerized *cis*-prop-1-enyl gradually increases as the reaction temperature increases. Interestingly, at the same temperature, the nature of the reaction conditions did not significantly affect the extent of isomerization with similar values being obtained for polymerizations in solution, and under melt conditions. Finally, there was no evidence from either ^{1}H or ^{13}C NMR spectroscopy that the deprotonated allyl-ether side-chains react nucleophilically with AGE monomer leading to branching and the conclusion that the deprotonated allyl side chains are transient and non-nucleophillic species.

Having noted that the extent of *cis*-prop-1-enyl isomer formation was related to reaction temperature, several neat polymerizations were carried out at fixed polymerization times (20 h) between 40 and 140 °C in 20 °C increments with the degree of isomerization being characterized by ^{1}H NMR spectroscopy (Fig. 5). For neat polymerizations carried out at lower temperatures (40 °C), very low levels of isomerization are observed (1.5% mol) which increases on progressing to 80 °C (3.7% mol) followed by a significant increase in the level of isomerization for neat polymerizations carried out above 100 °C (8.3–16.6% mol). The mole percent of *cis*-prop-1-enyl isomers that resulted from neat polymerizations carried out at 40–140 °C are shown in Table 2.

Heatley et al.[20] investigated the isomerization of allyl ethers to propenyl ethers that occurs during the oxyanionic polymerization of propylene oxide as a side reaction. Through a detailed analysis by ^{1}H NMR spectroscopy, the authors came to the conclusion that the activation energy for the allyl to *cis*-prop-1-enyl isomerization was 116 kJ/mol. For a bimolecular reaction between a living chain end and an allyl group, the rate of isomerization is given by $-\mathrm{d[Allyl]}/\mathrm{d}t = k\,[\mathrm{Allyl}][\mathrm{ROK}]$, with the temperature dependent rate constant given by:

$$\ln k = 26.31 - 13,960/T(\mathrm{L\ mol^{-1}\ s^{-1}}) \qquad (1)$$

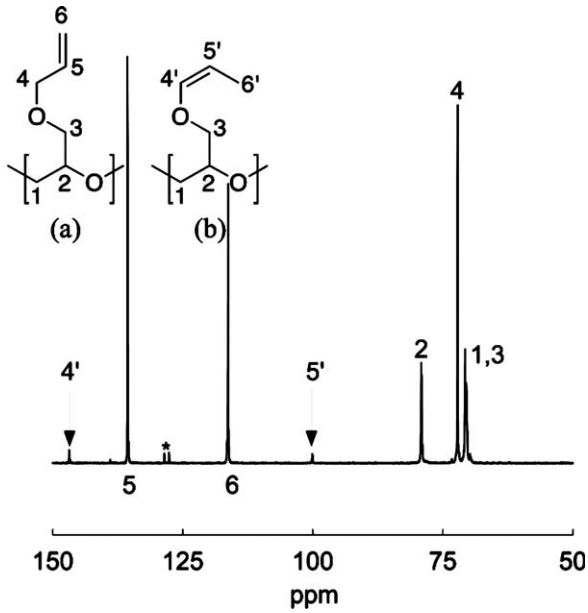
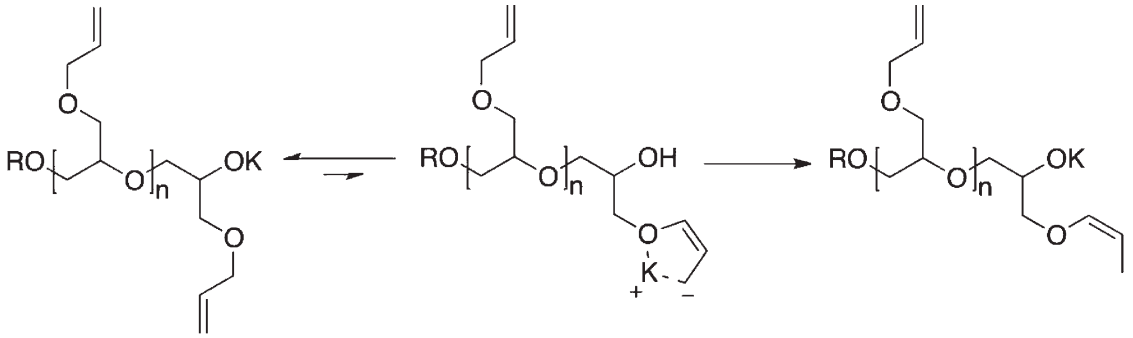


FIGURE 4 ^{13}C NMR spectrum of PAGE polymerized neat at 120 °C (see Table 2). Repeat unit isomers are shown with assignments in (a) and (b). Resonances due to carbon atoms in the benzyl end group are indicated with an asterisk.



SCHEME 2 Proposed isomerization of allyl-substituents to *cis*-prop-1-enyl units.

Using the integrated rate law and assuming the density of PAGE is 1.0 g/mL, for a fixed reaction time of 20 h, the incorporation of isomers would be expected to increase precipitously above 100 °C based on the rate constant determined by Heatley et al. Although the concentration of allyl groups Heatley et al. used in their analysis was significantly lower than that for PAGE, their kinetics for allyl to *cis*-prop-1-enyl isomerization agree qualitatively with the temperature dependence of allyl to *cis*-prop-1-enyl isomerization occurring in AGE during neat polymerization.

Obermeier and Frey briefly addressed the issue of allyl-ether isomerization in copolymerizations of AGE and ethylene oxide.[13] A very broad range of isomerization values (0–10 mol %) was reported for polymerizations carried out even at 40 °C. This is in contrast to our results where a polymerization temperature of 100 °C resulted in 8 mol % cis-prop-1-enyl isomers, and 30 °C results in undetectable levels of isomerization along the PAGE backbone. It is difficult to speculate on the origins of this difference. However, the potassium naphthalenide system that we employ for the polymerization of AGE yields reproducibly undetectable levels of isomerization for melt polymerization carried out below 40 °C up to molar masses as high as 90 kg/mol explored in this study which suggests another advantage for this polymerization system when compared to other alkoxide (cesium) systems.

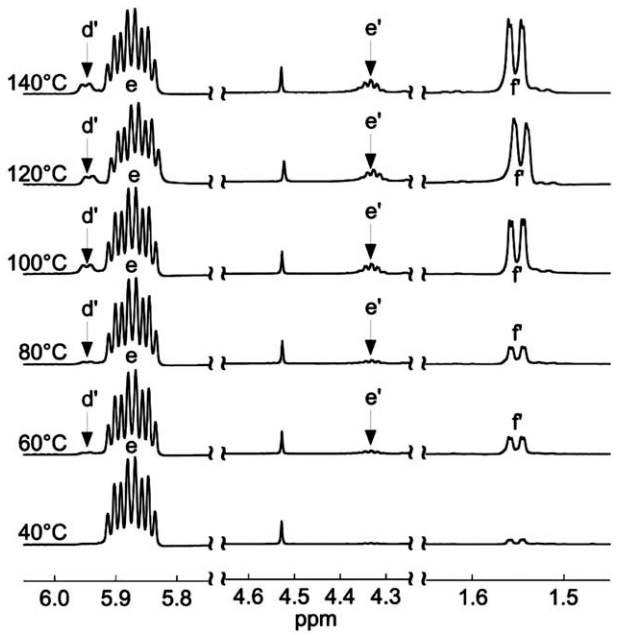


FIGURE 5 ^{1}H NMR spectra resulting from polymerizations carried out at various temperatures (40–140 °C). All spectra are normalized to the intensity of the benzyl resonance near 4.5 ppm (2H), and peak-assignments are shown in Figure 3. The mole percent incorporation of *cis*-prop-1-enyl isomers increases with polymerization temperature for polymerizations of equivalent duration as evidenced by the increase in intensity of the peaks due to the d′ (1H), e′ (1H), and f′ (3H) protons.

A detailed understanding of the isomerization of AGE during polymerization at elevated temperatures opens the opportunity to exploit the reactivity of the resulting *cis*-prop-1-enyl groups which are hydrolytically unstable and can give rise to hydroxyl groups. Indeed, the examination of the ^{1}H and ^{13}C NMR spectra of PAGE materials containing *cis*-prop-1-enyl isomers revealed an apparent loss in the number of prop-1-enyl groups relative to backbone ether protons on exposure to hydrolytic conditions. This discrepancy was correlated to the degree of isomerization of each sample and in most cases surpassed the amount of remaining *cis*-prop-1-enyl

TABLE 2 Isomerization of Allyl Groups During Neat Polymerization of AGE at 40–140 °C

$T_{polym.}$[a]	M_n[b]	M_n[c]	PDI[d]	%Isomer[e]
40	17.2	17.4	1.09	1.5
60	18.7	19.2	1.11	3.9
80	16.8	17.2	1.11	3.7
100	14.0	14.4	1.14	8.3
120	15.7	17.5	1.19	16.3
140	14.8	16.4	1.20	16.6

[a] Polymerization temperature in °C.
[b] Molar mass in kg/mol, determined by the allyl protons using ^{1}H NMR spectroscopy.
[c] Molar mass in kg/mol determined by the backbone-ether protons using ^{1}H NMR spectroscopy.
[d] Determined by RI-SEC in chloroform relative to polystyrene standards.
[e] Mole percent of *cis*-prop-1-enyl ether units determined by ^{1}H NMR spectroscopy.

isomer. Ishizaki et al.[21] reported that allyl ethers can be deprotected to alcohols via catalytically generating *in situ* the labile *cis*- and *trans*-prop-1-enyl isomers in a protic solvent (e.g., methanol) under mildly basic conditions.[22] These conditions are similar to those present during termination of the polymerization reaction with protic solvents.

The flexibility of PAGE as a molecular platform is enhanced by this controlled formation of *cis*-prop-1-enyl groups and can be specifically exploited.[19] For example, reaction of PAGE containing ~13% (mol.) *cis*-1-Propenyl isomer in methanol over a polymer-supported sulfonic acid resin (DOWEX) results in quantitative cleavage of the *cis*-1-propenyl groups to hydroxy functionalities. This affords a linear random copolymer of glycidol and AGE and provides a mechanism for orthogonal modification of the PAGE backbone via the hydroxy- and allyl-functionalities. Significantly, the amount of *cis*-1-propenyl isomerization may be tuned by the reaction conditions; lower temperatures generally result in lower levels of isomerization (see Tables 1 and 2 and Fig. 5) for the same polymerization time.

EXPERIMENTAL

Materials

All chemicals were used as received from Sigma-Aldrich unless otherwise specified. THF was collected from a dry solvent system and used immediately thereafter. Benzyl alcohol was dried over calcium hydride and distilled before titration with potassium naphthalenide in THF. AGE (TCI-America) was degassed through several freeze-pump-thaw cycles and distilled from butyl magnesium chloride to a preweighed and flame-dried buret immediately before use. Potassium naphthalenide was prepared from potassium metal and recrystallized naphthalene in dry THF and allowed to stir with a glass-coated stir-bar for 24 h at room temperature before use.

Characterization

^{1}H NMR spectroscopy was carried out on a Bruker AC 500 spectrometer in deuterated chloroform. ^{13}C NMR spectroscopy was carried out on neat PAGE containing a sealed D_2O capillary containing for locking and shimming the spectrometer. Size exclusion chromatography (SEC) was performed on a Waters chromatograph with four Viscotek colums (two I-MBHMW-3078, I-series mixed bed high molecular weight columns and two I-MBLMW-3078, I-series mixed bed low-molecular weight columns) for fractionation, a Waters 2414 differential refractometer and a 2996 photodiode array detector for detection of eluent, and chloroform with 0.1% tetraethylamine at room temperature was used as the mobile phase. Gas chromatography was carried out on a Shimadzu GC-2014 using a flame ionization detector and a Restek column (SHRXI-5MS) for separation.

Polymerizations and Modifications

All polymerizations were carried out on a Schlenk line in custom thick-walled glass reactors fitted with threaded ACE-threads under an argon atmosphere. The reactors were dried under vacuum then refilled with argon five times. Under an argon atmosphere, benzyl alcohol initiator was added by gas-tight syringe through a 6-mm puresep septum. Potassium alkoxide initiators were formed by titration of benzyl alcohol with potassium naphthalenide under argon until a green color persisted in solution indicating the deprotonation of all alcohols. Two polymerization procedures were followed: (A) Bulk polymerizations were carried out between 30 and 140 °C for 20 h and terminated with methanol. (B) Solution polymerizations were carried out in diglyme between 30 and 140 °C for 20 h and terminated with methanol. Polymerizations carried out at higher temperatures (>100 °C) were carried out on small scales (ca. 1 g). Deprotection of the *cis*-prop-1-enyl ether isomers was carried out in methanol using five equivalents of DOWEX resin by mass. Complete conversion of the *cis*-prop-1-enyl ethers to hydroxyls was observed by complete disappearance of all ^{1}H NMR signals consistent with the *cis*-prop-1-enyl ethers. For the synthesis of PAGE with undetectable levels of isomerization, controlled molar masses, and low PDIs, polymerization in the melt at 30 °C was carried out for 20–144 h depending on the target molecular weight.

^{1}H NMR of PAGE (500 MHz, $CDCl_3$): δ 1.55 (d, —O—CH=CH—CH_3), 3.47–3.72 (broad m, —O—CH_2—CH(CH_2—O—CH_2—CH=CH_2) —O— and —CH_2—CH(CH_2—O—CH=CH—CH_3)—O—), 3.79/3.87 (two broad peaks, —CH_2—CH(CH_2—O—CH=CH—CH_3)—O—), 4.01 (d, —O—CH_2—CH=CH_2), 4.38 (m, —O—CH=CH—CH_3), 4.56 (s, Ph-CH_2—O—), 5.18/5.28 (doublet of doublets, —O—CH2—CH=CH_2), 5.91 (m, —O—CH_2—CH=CH_2), 5.97 (d, —O—CH=CH—CH_3), 7.30 (overlap with residual $CHCl_3$, 1H on Ph—CH_2—O—), 7.36 (s, 4H on Ph—CH_2—O—). ^{13}C NMR of PAGE (500 MHz, neat PAGE, D_2O capillary for shimming): δ 70.9 (—O—CH_2—CH(CH_2—O—CH_2—CH=CH_2)—O—), 72.0 (—O—CH_2—CH=CH_2), 79.4 (—O—CH_2—CH(CH_2—O—CH_2—CH=CH_2)—O—), 100.3 (—O—CH=CH—CH_3), 116.3 (—O—CH_2—CH(CH_2—O—CH_2—CH=CH_2)—O—), 127.5/128.6 (5C, Ph—CH_2—O—), 135.6 (—O—CH_2—CH(CH_2—O—CH_2—CH=CH_2)—O—), 138.8 (1C, Ph—CH2—O—), 146.8 (—O—CH_2—CH(CH_2—O—CH=CH—CH_3)—O—).

CONCLUSIONS

The polymerization of AGE using potassium alkoxide initiators has been shown to result in low polydispersity, controlled molecular weight materials under both solution and melt conditions. Depending on the specific polymerization temperature, either no isomerization of the allyl groups was observed (30 °C) or the fraction of allyl groups along the backbone isomerized into labile *cis*-prop-1-enyl groups was found to increase with increasing reaction temperature. Significantly, hydrolysis of the isomerized *cis*-prop-1-enyl groups to hydroxyl groups could be achieved by a postpolymerization treatment giving orthogonally reactive hydroxy and allyl groups along the backbone. The properties and inherent chemical functionality of the resultant PAGE material makes it amenable as a polymeric platform with potential applications in a wide range of technological areas.

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